

Langley



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
WASHINGTON, D.C. 20546

November 19, 1970

REPLY TO  
ATTN OF: GP

TO: USI/Scientific & Technical Information Division  
Attention: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General Counsel for  
Patent Matters

SUBJECT: Announcement of NASA-Owned U. S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code USI, the attached NASA-owned U. S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U. S. Patent No.	: 3,521,054
Government or Corporate Employee	: GCA Technology Division A Division of GCA Corporation Bedford, Mass. 01730
Supplementary Corporate Source (if applicable)	: _____
NASA Patent Case No.	: LAR-10180-1

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:

Yes ☒

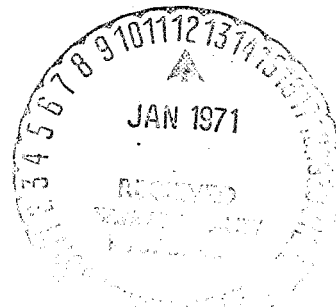
No ☐

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of Column No. 1 of the Specification, following the words "... with respect to an invention of . . . ."

*Elizabeth A. Carter*  
Elizabeth A. Carter

Enclosure

Copy of Patent cited above



COSATI 07D

(CATEGORY)

July 21, 1970

JAMES E. WEBB

3,521,054

ADMINISTRATOR OF THE NATIONAL AERONAUTICS  
AND SPACE ADMINISTRATION

ANALYTICAL PHOTOIONIZATION MASS SPECTROMETER WITH AN ARGON  
GAS FILTER BETWEEN THE LIGHT SOURCE AND MONOCHROMETER

Filed Feb. 29, 1968

2 Sheets-Sheet 2

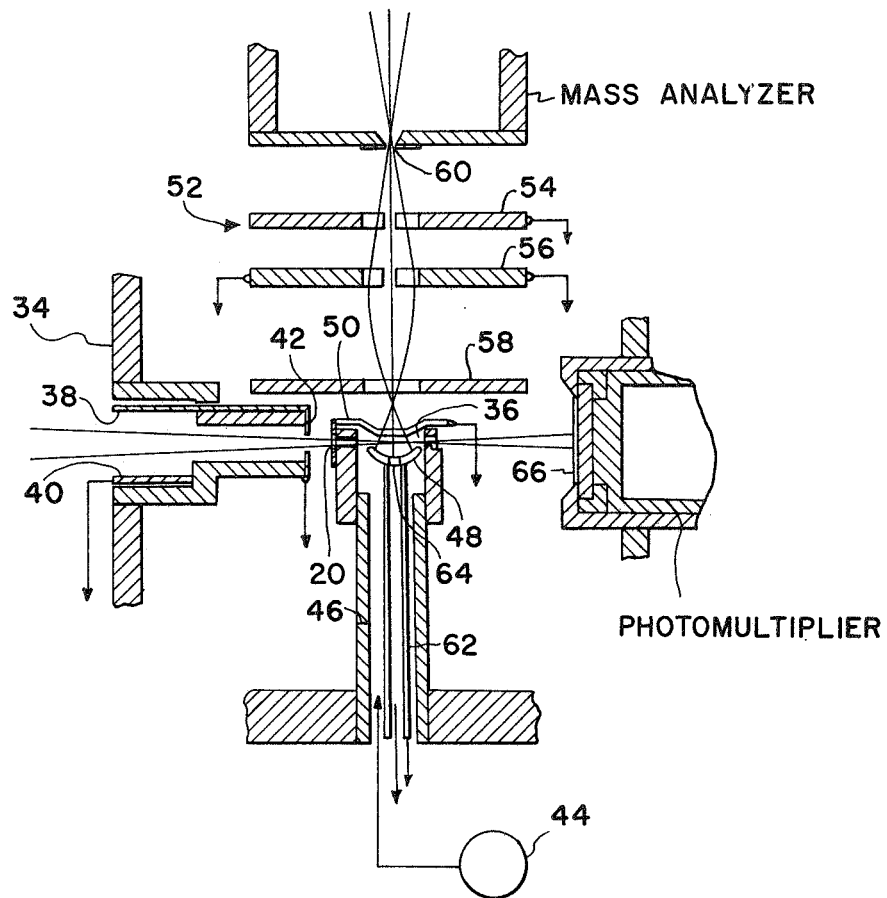


FIG. 2

INVENTORS  
WALTER P. POSCHENRIEDER  
JAMES A. R. SAMSON  
BY PETER WARNECK  
*9/11/70*  
*Howard J. Osburn*  
ATTORNEYS

1

3,521,054

## ANALYTICAL PHOTOIONIZATION MASS SPECTROMETER WITH AN ARGON GAS FILTER BETWEEN THE LIGHT SOURCE AND MONOCHROMETER

James E. Webb, Administrator of the National Aeronautics and Space Administration, with respect to an invention of Walter P. Poschenrieder, Burlington, James A. R. Samson, Waltham, and Peter Warneck, Bedford, Mass.

Filed Feb. 29, 1968, Ser. No. 709,398

Int. Cl. B01d 59/44; H01j 39/34

U.S. Cl. 250—41.9

4 Claims

### ABSTRACT OF THE DISCLOSURE

A mass spectrometer of the type utilizing photoionization to produce ions of the sample analyzed, featuring a device for producing an ionizing light beam of any of a range of wavelength values consisting of the combination of a multi-lined spectrum source, an adjustable angle diffraction grating, and a filtering element that removes the portion of the multi-lined spectrum that shows up as second order interference on the selected portion of the first order spectrum, thus insuring discriminatory ionization. A specific embodiment is disclosed that is useful for detection of pollutants in natural air by providing a light beam source that can discriminately ionize pollutants in a mixture with the naturally-occurring masking constituents.

The invention disclosed herein may be manufactured and used by or for the Government of the United States of America without the payment of royalties thereon or therefor.

This invention relates to a mass spectrometer, and more particularly to a mass spectrometer incorporating a photoionization arrangement for bringing about the necessary ionization of the sample gas.

The principles and theoretical advantages of the use of the photoionization with a mass spectrograph or spectrometer are well established. The basic difference is the substitution of a light beam as the source of ionizing energy, instead of the usual electron beam. One resulting improvement of interest here is in the much bettered capability of accurately controlling the ionization energy applied to the test sample by varying the wavelength of the radiation forming the ionizing light beam, since the intensity of the usual electron beam arrangement is very difficult to control. This makes possible a discriminatory ionization of molecules having substantially identical masses, but slightly differing ionization potentials, such as is the case with CO and N<sub>2</sub>, ultimately resulting in greatly enhanced sensitivity of such analyzers to concentrations of one of these gases in the other. Since only very elaborate and cumbersome mass spectrometers using an electron beam ionizing mechanism can so distinguish, a much simpler and lighter device having this capability could result. Practical development of the concept focused on the need for a photoionizing beam source which could controllably produce wavelengths of a selected value, since one of the great advantages, discriminatory ionization, of course necessarily relied on such a capability. The simplest solution would of course be the use of a light source which would emit only wavelengths of a pre-selected desired value. In actual fact, however, such a source is unavailable. Resonance light sources, while producing emissions of discrete wavelengths, are limited to that which is naturally-occurring, and, hence, does not yield a great deal of flexibility. The lack of control over the emissions of such sources limits the flexibility of the

2

instrument further, as scanning of a wavelength range is impossible. Other possible arrangements for directly producing wavelengths of preselected values in general suffer from these same drawbacks.

A second approach provided a photoionizing beam source consisting of a light source producing either a multilined or continuous spectrum corresponding to energy levels in the range of the ionization potentials of the sample gases of interest. The output of the light source was then directed to an adjustable-angle diffraction grating, and thence to the ionizing chamber of the mass analyzer. This arrangement provided in theory both flexibility and control over the energy level of the ionizing beam allowed to enter the ionizing chamber. However, it was found that even though the energy level of the light theoretically being directed to the ionization chamber of the mass spectrometer was of a level below that required to ionize a particular gas present in the test sample, significant ionization of such gases did occur, with resulting impairment of the sensitivity of the instrument in distinguishing such gases from others present having the same mass number. With research it was found that such undesired ionization came about because of the presence of scattered light of differing wavelength and also because of interference of higher order lines. In the described situation, the transmission of the higher order lines, superimposed on the first order lines resulted in the entrance to the ionizing chamber of significant amounts of radiation of sufficient energy to ionize gases which the selected first order wavelengths were incapable of so doing, thus leading to the inaccuracies described.

No technical gratings are known which only or preferentially produce a first order spectrum, and it also is not practical to reduce the effect of scattering on grating irregularities and other system elements to an acceptable degree.

These difficulties prevented the widespread practical application of the photoionization mass spectrometer to such uses as an air pollution measurement device, which was unfortunate since commonly found pollutants as, for example, carbon monoxide, are masked from the conventional mass spectrometer by naturally-occurring constituents having the same mass number and of much higher relative concentrations.

Therefore, it is an object of the present invention to provide a relatively simple mass spectrometer which effectively discriminates between test samples of substantially similar mass numbers having differing ionization potentials.

It is another object of the present invention to provide an improved photoionization mass spectrometer which discriminately ionizes only test samples having selected ionizing potentials.

It is a further object of the present invention to provide a photoionization mass spectrometer which has a high degree of flexibility in selecting applied ionizing energies, yet produces an ionizing beam free from wavelengths of nonselected energy levels.

It is yet another object to provide a relatively simple mass spectrometer which has the capability of detecting pollutants in air which are masked by naturally-occurring constituents.

It is still another object of the present invention to provide a photoionization mass spectrometer which has the flexibility to scan both the range of mass numbers and ionization potentials of commonly found air pollutants while retaining a high degree of discriminatory capability between elements of the same mass number and differing ionization potentials.

These and other objects which will become apparent upon an examination of the specification and claims are

in general accomplished by providing a photoionization mechanism for a mass spectrometer by combining a light source having a multiline or continuous spectrum output with an adjustable-angle diffraction grating, and including a filter element to remove all radiation that appears at the selected diffraction angle in the form of second or higher order spectra.

In the drawings, FIG. 1 is a diagrammatic view of the basic combination, showing in partial section the photoionizing beam source.

FIG. 2 is a sectional view of the ionization chamber and related structure.

FIG. 3 is a fragmentary view of a partial section of an alternative filter arrangement.

FIG. 4 is a fragmentary view of a partial section of another alternative filter arrangement.

Referring now to the drawings and particularly FIG. 1, the basic combination consists of a mass analyzer which is combined with a source of a test sample gas and an ionizing chamber to provide a supply of ions of the sample gas for acceleration into, and collection, measurement, etc., in the mass analyzer.

This instrument operates in a well known manner to produce a mass spectra of positive ions of the test gas, and it is not thought necessary to describe and show in detail the instrument. In general, the test gas ions are accelerated and projected into the mass analyzer at a given velocity. They then move through a magnetic field in the analyzer and magnetic forces tend to direct them into a curved path, the mass of the ion and its initial velocity controlling the amount of deviation it undergoes in passing through the magnetic field. An exit slit and an ion detector are positioned at a point so as to collect ions having a certain value of mass for a given initial velocity, and thus by controlling the initial velocity, a mass spectrum may be scanned.

The mass analyzer may be of conventional design, although some types are more suited than others for application in a photoionization type of mass spectrometer, in view of the small numbers of ions produced by a photo ion source compared with an electron impact ion source. This situation means extremely desirable an instrument having a very high transmission, while retaining as high a resolution as possible. The most suitable solution to these needs is a 180-degree magnetic analyzer which utilizes an inhomogeneous magnetic field between a wedge-shaped air gap. This instrument is well known in the prior art and has been described in the literature and as it in itself forms no part of the present invention, it is not felt necessary to show or describe it in detail.

The arrangement for producing the photionizing beam is indicated generally at 10, and is arranged to direct its output to the ionization chamber in communication with a source of a sample gas and the mass spectrometer. The photoionizing beam source 10 is composed of three general elements, a light source 12, a filter unit 14, and an adjustable diffraction grating monochromator 16.

It should be noted at this point that the particular embodiment to be described is intended to be utilized to detect pollutants in air, and as such, these various elements are so designed to produce ionization energy levels of the general range required to ionize these gases, and to distinguish from the naturally-occurring constituents of the atmosphere, but the inventive concept is to by no means be limited to such a particular application.

With the above application in mind, the light source 12 was chosen to be a pulsed spark light using argon gas. Since this device is well known, as evidenced by the article "Photoionization Analysis by Mass Spectroscopy," J. Opt. Soc. Am. 49, 338-349, it is not felt necessary to fully describe it, but merely suffice it to say that it generally consists of an arrangement whereby spark pulses in an argon atmosphere produces a rich spectrum of widely spaced lines in the region of 400 A. to 1000 A. This range covers the energy levels required to ionize many of the commonly

found toxic pollutants in the atmosphere, and therefore was considered as an acceptable light source for the purpose herein referred to. For wavelengths over 1000 A., a hydrogen continuous discharge light source can be used, which delivers a multiline spectrum of sufficient intensity at wavelengths larger than 1000 A.

The particular location of the gas filter element 14 in the path of the light beam to the ionization chamber is theoretically immaterial as to its filtering function, but certain practical considerations warrant its location as shown. No solid windows are known which can be used below 1040 A. to seal the ends of the filter cell, and therefore leakage of gas must be present into the evacuated portions of the instrument. Hence, in order to minimize leakage and the effect of the aperture of the light beam the placement of the filter element 14 should be either adjacent the entrance slit 18 or the exit slit 20. Further considerations preclude any placement of the filter element 14 adjacent the exit slit 20, at least for the gas filter species shown in FIGS. 1 and 3, since, as will be described herein high electric potentials are present in this area and there would be a consequent danger of glow discharges. Further, the proximity of the gas type filter element 14 to the ionization chamber would also cause flow of filter gas therein and obscure the spectrum of the sample gas. Thus, placement on one or the other side of the entrance slit 18 is considerably more advantageous, and further considerations of loss of intensity of the light beam and possible problems due to mixing of filter and spark pulse gas lead to the final location of the filter element between the entrance slit 18 and the diffraction grating 22.

The actual construction of the filter cell 14 is comparatively simple, as shown in FIG. 1. The partition for the entrance slit 18 and a second partition 24 form a cavity 26, which is filled with a gas through an entrance 28 from a source 30. The length of the cavity, the density of the gas contained therein, and the absorption spectra of the particular gas all affect the filtering characteristics, i.e., the amount and the spectra of absorption of a light beam passing through. Since the gases may be conveniently changed or mixed, it can be seen that this type of filter provides a good deal of flexibility in its operating characteristics.

The functioning of the filter unit in this combination can best be explained by reference to the actual parameters of the specific embodiment disclosed, together with its application to two exemplary gases, CO and N<sub>2</sub> both having mass numbers of 28, and ionization potentials corresponding to 835 A. and 795 A. respectively. For this particular application, argon gas displays an absorption spectra having a sharp cutoff at 788 A. Therefore, scattered light of shorter wavelength than 788 A. is eliminated. More importantly however, the second order line of 419 A. at the diffraction angle producing a first order line of 838 A. is eliminated. Thus, when the CO ionization potential corresponding to 835 A. is scanned, the elimination of the high energy 419 A. also eliminates the heretofore extensive unwanted ionization of N<sub>2</sub>, while still allowing scanning of the first order wavelength corresponding to the ionization potential of N<sub>2</sub> at 795 A. Hence, it can be seen that the discriminatory capability of the instrument has been much enhanced, while retaining a flexible scanning ability by a careful selection of the combination of a light source and filtering agent with an adjustable diffraction grating.

The nonabsorbed light beam is then directed to the adjustable-angle diffraction grating 22 which serves to disperse the impinging radiation at various angles depending on the wavelength in a well known fashion, and selectively directs a portion of the resulting spectrum to the exit slit 20. The adjustment mechanism indicated at 32 precisely controls the angle of the grating 22 with respect to the entrance and exit slits 18 and 20, and therefore precision control over the portion of the spec-

trum so directed is provided and in turn the energy level of the photoionizing beam is controlled. A vacuum pump 33 maintains a low pressure within the monochromator.

The details of the photoionization ion source and the related monochromator structure is shown in FIG. 2. The housing 34 of the monochromator is arranged so that the dispersed light beam reflected from the diffraction grating 22 passes through the exit slit 20, and enters the photoionization chamber 36. In so doing, the beam first passes between two electron deflector plates 38 and 40 and through an aperture disc 42. Plate 38 and disc 42 are maintained at a potential about 100 volts more positive than that of the ion source, while plate 40 is maintained at ground potential. This structure is necessary in the embodiment incorporating the gas filter 14, since the use of this element leads to higher pressures in the monochromator 16, which in turn leads to significant photoelectron production. With the arrangement shown no electrons can pass into the ionization chamber 36 from the monochromator 16.

The light beam then enters the ionization chamber 36 through the slit 20, where it encounters molecules of the sample gas which has been transmitted to the chamber 36 from a source 44 through the tube 46. A special concave repeller plate 48, which is maintained at a high positive potential, accelerates the ions formed by the light beam towards the extraction electrode 50, which is convex with respect to the beam, for the same purpose. The radial electrical field produced by the shape of these electrodes directs all the ions in its filed into the immersion lens systems 52, resulting in a higher available ion current, which as has been mentioned, is a critical area of photoionization mass spectrometers. The immersion lens system 52 accelerates and focuses the ions directed toward it onto the mass spectrometer entrance slit 60, and is composed of three plates 54, 56, and 58 having openings therein. The potential of the first plate 58 affects the focal length of the ion beam, while the following two plates are divided into halves and permit adjustment of the ion beam in vertical and horizontal directions. These two plates are kept on a negative potential with respect to ground, and therefore, secondary electrons conceivably formed by interaction of the ion beam with the spectrometer entrance slit 60 are prevented from being accelerated back into the ion source.

The pressures in the ionization chamber may be maintained through a central tube 62 and an opening 64 in the repeller plate 48.

After the light beam has passed through the ionization chamber 36, it falls on a sodium salicylate coated window 66, which is viewed by the photomultiplier. This provides a simple and convenient light beam monitor.

Alternative filter arrangements are shown in FIGS. 3 and 4. In FIG. 3, a gas filter arrangement is still employed, but a buffer chamber 68 is added by the addition of a partition 70, an outlet 72, and a pump 74. The pump 74 may be used to either provide differential pumping between 30 and 74, thereby minimizing flow into the monochromator 16, or to augment 30 by pumping in parallel. This improves flexibility of the filter, since the pressure therein may be more readily varied, and also may be used to lessen its effect on the monochromator.

A thin film metal filter is shown in FIG. 4. For the use contemplated for the embodiment disclosed, a thin film of indium was considered as a satisfactory filtering agent, since it displays a rather sharp cutoff at 750 Å., while allowing relatively good transmission from 800 Å.-1000 Å. Thus second order interferences as well as short wavelength scattered light are eliminated, and scanning over this range can be accomplished while maintaining a relatively high degree of purity of wavelength of the light directed to the ionization chamber. This film, of a thickness of the order of 3000 Å., indicated at 76, is placed just ahead of the entrance slit 18, and may be mounted in a

frame 78 pivotally secured to partition 80, by a connection 82, allowing the film to be moved in and out of the light beam path. The transmission of the film 76 is not high, and therefore location as close as practicable to the light source is important in order to maintain a reasonable intensity of the ionizing beam.

From the above description, it can readily be appreciated that a photoionization mass spectrometer of much improved characteristics has been provided. The range of wavelengths emitted by the light source and the adjustable diffraction grating, combined with the filtering element, allows extremely effective discriminatory scanning of an ionization potential range for a given mass setting on the mass spectrometer. This yields a flexible, simple, and extremely accurate mass spectrometer capable of distinguishing a range of compounds or elements having similar mass numbers with slightly differing ionization potentials.

Furthermore, a specific embodiment has been provided which can detect a number of common pollutants, such as CO, in natural air having masking constituents, such as N<sub>2</sub>, in much higher concentrations. By scanning both the mass range of the mass spectrometer, and the ionization potential range, a mixture of air can effectively be analyzed for a series of trace pollutants by equipment much simpler and lighter than that used in the past.

Finally, while the design of the embodiments disclosed have been particularly directed to use as an air pollutant analyzer, the invention is not to be so limited, but may be directed to different applications, which may lead to re-design for ionization potential ranges corresponding to wavelengths well over 1000 Å., in turn calling for a different light source, filtering element, etc. Furthermore, many alternative filtering agents could be utilized, such as the creation of higher pressures in the light source itself to induce self-absorption, or the use of other types of filtering materials, or even the compounding of monochromators in order to eliminate the described portions of the emitted spectra. Thus, the invention is to be limited only by the following appended claims.

What is claimed is:

1. A photoionization mass spectrometer comprising: a mass analyzer means for determining the mass spectrum of ions projected therein; an ionization chamber; means for projecting ions present in the said ionization chamber into said mass analyzer; a pulsed spark in an argon atmosphere light source emitting light having a range of wavelength values; a vacuum monochromator including a diffraction grating means positioned to intercept a portion of said emitted light and diffract it at various angles as a function of its wavelength; means for directing a selective portion of said diffracted light into said ionization chamber; and a filter means including a chamber enclosing a volume of argon gas positioned at a point in the path of the light from the source to the ionization chamber for removing any portion of the range of wavelength values emitted by the said light source that is diffracted as higher order radiation along substantially the same path as the selected portion.
2. The photoionization mass spectrometer of claim 1 wherein said chamber includes a partitioned smaller cavity proximate said monochromator in communication therewith for improving the flexibility of said filter means and means for evacuating said smaller cavity.
3. The photoionization mass spectrometer of claim 1 wherein said means for directing a selective portion of said diffracted light into said ionization chamber includes means selectively adjusting the angle of said diffraction grating relative to said light source.

4. A photoionization mass spectrometer comprising:  
a mass analyzer means for determining the mass spectrum of ions projected therein;  
an ionization chamber;  
means for projecting ions present in the said ionization chamber into said mass analyzer;  
a pulsed spark in an argon atmosphere light source emitting light having a range of wavelength values;  
a vacuum monochromator including a diffraction grating means positioned to intercept a portion of said emitted light and diffract it at various angles as a function of its wavelength;  
means for directing a selective portion of said diffracted light into said ionization chamber, and  
a chamber enclosing a volume of argon gas positioned in the path of the light from the spark pulse source to the ionization chamber for filtering said light.

**References Cited****UNITED STATES PATENTS**

2,772,362 11/1956 Dietz ----- 250—41.9

**OTHER REFERENCES**

"Photon Impact Studies of Molecules Using A Mass Spectrometer," by H. Hurzeler et al., from "The Journal of Chemical Physics," vol. 28, No. 1, January 1958, pp. 76-79.

"Photoionization Analysis by Mass Spectroscopy," by G. L. Weissler et al., from the "Journal of the Optical Society of America," vol. 49, No. 4, April 1959, pp. 338-340.

WILLIAM F. LINDQUIST, Primary Examiner